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Nonlinear eigenvalue problems in Density Functional Theory calculations

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Developed in the 1960's by W. Kohn and coauthors[1, 2], Density Functional Theory (DFT) is a very popular quantum model for First-Principles simulations in chemistry and material sciences. It allows calculations of systems made of hundreds of atoms. Indeed DFT reduces the 3N-dimensional Schroedinger electronic structure problem to the search for a ground state electronic density in 3D. In practice it leads to the search for N electronic wave functions solutions of an energy minimization problem in 3D, or equivalently the solution of an eigenvalue problem with a non-linear operator.

We consider the Density Functional Theory energy functional written as a functional of N orthonormal electronic wave functions ψ_i (Kohn-Sham formulation)

$$(1) \quad E_{KS}[\{\psi_i\}_{i=1}^N] = \sum_{i=1}^N \int_{\Omega} \psi_i(x) (-\Delta \psi_i)(x) dx + \int_{\Omega} \int_{\Omega} \frac{\rho(x_1)\rho(x_2)}{|x_1 - x_2|} dx_1 dx_2 \\ + E_{XC}[\rho] + \sum_{i=1}^N \int_{\Omega} \psi_i(x) (V_{ext} \psi_i)(x) dx$$

where ρ is the electronic density defined by

$$(2) \quad \rho(x) = \sum_{i=1}^N |\psi_i(x)|^2$$

(see for example [3]). E_{KS} is made of the sum of the kinetic energy of the electrons, the Coulomb interaction between electrons, the exchange and correlation electronic energy, and the energy of interaction of the electrons with the potential generated by all the atomic cores V_{ext} . Given an external potential V_{ext} — defined by the various atomic species present in the problem, their respective positions and pseudopotentials — the ground state of the physical system is obtained by minimizing the energy functional (1) under the orthonormality constraints

$$(3) \quad \int_{\Omega} \psi_i(x) \psi_j(x) = \delta_{ij}, i, j = 1, \dots, N.$$

To avoid mathematical difficulties irrelevant in the discussion of the numerical solver, let us assume that we have a problem in a finite dimensional space of dimension M resulting from the discretization of the above equations. To be concrete, suppose that we have a finite difference discretization on a uniform mesh with periodic boundary conditions, and thus the functions ψ_i are M -dimensional vectors with components corresponding to their values at the mesh points, $\psi_{i,k} = \psi_i(x_k)$. Let L_h be a finite difference approximation of the Laplacian operator. Without restriction of generality, wave functions are assumed to take real values only.

One can derive the Euler-Lagrange equations associated to the minimization problem (1) with N^2 Lagrange parameters corresponding to the orthonormality

constraints (3). One obtains the so-called Kohn-Sham (KS) equations in their usual form for the particular choice of the functions $\{\psi_i\}_{i=1}^N$ which diagonalizes the matrix of the Lagrange parameters,

$$\begin{cases} -L_h\psi_i + V_{KS}[\rho]\psi_i &= \lambda_i\psi_i \\ \rho(x_k) &= \sum_{i=1}^N |\psi_i(x_k)|^2 \\ \sum_{k=1}^M \psi_i(x_k)\psi_j(x_k) &= \delta_{ij} \end{cases}$$

where V_{KS} is a discretized nonlinear effective potential operator (see *e.g.* [3]). In this approach, one has to find the N lowest eigenvalues $\lambda_i, i = 1, \dots, N$ and the corresponding eigenfunctions. We assume that $\lambda_{N+1} - \lambda_N > 0$.

We can represent the solution of the discretized problem as an M by N matrix

$$\Psi = (\psi_1, \dots, \psi_N).$$

Ψ represents the invariant subspace spanned by the eigenvectors associated with the N lowest eigenvalues. Other representations of that same subspace by N linearly independent vectors can be written as

$$\Phi = (\phi_1, \dots, \phi_N).$$

One can find an $N \times N$ matrix C such that $\Psi = \Phi C$. C satisfies $CC^T = S^{-1}$ where $S = \Phi^T \Phi$, the Gram matrix, is of rank N . Using the previous relations, the electronic density can be written in terms of the matrix elements of Φ and S^{-1} ,

$$\rho_k = \sum_{i,j=1}^N (S^{-1})_{ij} \Phi_{ki} \Phi_{kj}$$

where ρ_k denotes the value of the electronic density at the mesh point x_k . Also the KS equations for Φ can be rewritten as

$$(4) \quad -L_h \Phi + V_{KS}[\rho] \Phi = \Phi S^{-1} H_\Phi$$

where $H_\Phi = \Phi^T (-L_h + V_{KS}) \Phi$. In this formulation, unlike more traditional approaches which include an additional equation to enforces orthonormality, the columns of Φ constitute a general nonorthogonal basis of the trial invariant subspace.

In first-principles molecular dynamics simulations, the equations of Density Functional Theory need to be solved at every step to determine the forces acting on individual atoms and responsible for the dynamics. To obtain meaningful statistics, $O(10^5)$ steps are required. Thus an efficient solver is needed for the KS equations.

For finite differences approaches — or pseudo-spectral methods also very popular in the field —, about 1% of the eigenpairs of large sparse KS Hamiltonian operators are needed. In this context, the nonlinear problem — Eq.(4) — can be efficiently solved using a subspace preconditioned inverse iteration [4]. A good preconditioner can be obtained based on the observation that the Hamiltonian operator is a Laplacian plus a perturbation (potential) [5]. Close to convergence,

subspace preconditioned inverse iterations can be accelerated using a simple extrapolation scheme for Φ , using the approximations obtained at the previous m steps of the iterative solver,

$$\bar{\Phi}_k := \Phi_k + \sum_{j=1}^m \theta_j (\Phi_{k-j} - \Phi_k).$$

The columns of Φ are assumed to be normalized at each step. The coefficients $\theta_j, j = 1, \dots, m$ are obtained from a residual minimization condition. Small values of m (1 or 2) work well in practice. Numerical results demonstrate excellent convergence rate for large scale applications involving over a 1000 eigenpairs. Such an algorithm is compatible with recently proposed $O(N)$ complexity approaches where the searched subspace is represented by a set of functions strictly localized in real-space [6].

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